

Time scales of syn-eruptive volatile loss in silicic magmas  
quantified by Li-isotopes

J. Neukampf\*, B.S. Ellis, O. Laurent, L.K. Steinmann, T. Ubide, M. Oeser, T. Magna, S.  
Weyer, and O. Bachmann

\*Correspondence to: [julia.neukampf@erdw.ethz.ch](mailto:julia.neukampf@erdw.ethz.ch)

**This PDF file includes:**

METHODS

Tables S1 to S3

## **METHODS**

### **Major element measurements**

*Backscattered electron imaging by scanning electron microscope (SEM) and electron probe (EPMA) analyses* (Si, Na, Mg, Al, Ca, K, Sr, Ti, Fe, Ba) of plagioclase grains were obtained at the Institute of Geochemistry and Petrology, ETH Zürich. Profiles were measured from core to rim with 5 to 10 µm steps with standards every 30 to 40 measurements. All analyses were measured with 15 kV acceleration voltage, a beam diameter of 10 µm and a beam current of 20 nA with counting times of 20 s on peak and 10 s on background. All analyses were performed so that the mobile elements (Na, K) were measured first. To ensure measurement accuracy, in-house reference minerals (albite, anorthite and microcline) from the ETH collection were used as secondary standards and reproducibility was better than 5 %.

### **Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) mapping**

*Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) mapping* was undertaken at The University of Queensland Centre for Geoanalytical Mass Spectrometry, Radiogenic Isotope Facility (UQ RIF-lab). Plagioclase crystals embedded in 1-inch polished resin mounts were analyzed following a published mapping method (Ubide et al., 2015; Ubide et al., 2019). The analytical set up comprised an ASI RESolution 193 nm excimer UV ArF laser ablation system with a dual-volume Laurin Technic ablation cell, coupled to a Thermo iCap RQ quadrupole mass spectrometer. Ablation was performed in ultra-pure He to which Ar make-up gas with a trace amount of N<sub>2</sub> was added for efficient transport and to aid ionization. The mapping area was built by overlapping ablation lines to form a rectangular grid, using a 20x20 µm square-shaped laser aperture, 20 µm/s translation speed, 10 Hz repetition rate, 3 J/cm<sup>2</sup> fluence, and 1 µm overlap between lines. A baseline measurement of 20-30 s was programmed between lines. Pre-ablation of

the crystals using large, quick rasters (100  $\mu\text{m}$  spot, 200  $\mu\text{m/s}$  speed and 20 Hz repetition rate) was found to improve the subsequent mapping. The total dwell cycle was 115 ms, including maximized dwell time for  $^7\text{Li}$  (50 ms). The instrument was tuned with scans on NIST SRM 612 silicate wafer reference material. NIST SRM 612 silicate wafer was employed as calibration standard and silicon concentrations (homogenous throughout single crystals) obtained by EPMA for each of the plagioclase crystals as internal standard. Spatially registered, quantitative multi-elemental maps were built with Iolite (Paton et al., 2011) v2.5, using CellSpace (Paul et al., 2012). Accuracy and precision were monitored via analysis of BHVO-2G, BCR-2G and GSD-1G glasses as secondary standards, using the same parameters as for the unknowns. Accuracy was better than 5 % for Li and better than 10 % for all other analyzed elements. Limits of detection (Longerich et al., 1996) were at the sub-ppm level for Li as well as all other trace elements.

#### ***In situ* Lithium isotope analysis of plagioclase crystals by femtosecond laser ablation-MC-ICPMS**

For the *in situ* determination of Li isotope composition in plagioclase phenocrysts a femtosecond laser based ablation system (Spectra-Physics Solstice) coupled to a multi-collector-ICP-MS (Thermo-Finnigan Neptune Plus) at the Leibniz Universität Hannover, Germany, was used. The ablation beam had a pulse duration of ~100 fs and wavelength of 194 nm which was generated via frequency conversion from an infrared beam with 775 nm wavelength in an in-house built mirror and lens system and focused on the sample surface via a modified New Wave (ESI) stage combined with an optical microscope (Horn et al., 2006). The laser spot size of ~26  $\mu\text{m}$  on the komatiite reference glass wafer GOR132-G (MPI DING) allowed for sufficient spatial resolution. Isotope measurements were performed according to the published method of

Steinmann et al., (2019), by employing standard-sample-bracketing with the GOR132-G glass as a bracketing standard according to Equation 1 and recalculation to IRMM-16.

$$\delta ^7Li = \left[ \frac{\left( \frac{^7Li}{^6Li} \right)_{sample}}{\left( \frac{^7Li}{^6Li} \right)_{GOR132-G}} - 1 \right] \times 1000 \quad (1)$$

Due to low Li concentrations (5-30 ppm) in the plagioclase a device was implemented for gas flow homogenization into the tubing system behind the ablation cell to homogenize the ablated aerosol with the transport Helium gas. Afterwards the make-up Ar gas was added and the gas-aerosol mixture was transported to the mass spectrometer. The homogenization of the gas flow was necessary to enhance signal stability and decrease the analytical error. In order to decrease matrix effects by avoiding the ionization of matrix elements in the plasma, relatively cool plasma conditions (RF power 900 W) were applied. *In situ* Li isotope ratio measurements were performed in static mode at low mass resolution which is sufficient to resolve atomic interferences. In order to keep background Li signals low, the measurements were performed under dry plasma conditions. For the detection of  $^7Li$ , a Faraday cup equipped with a slow-response  $10^{13} \Omega$  amplifier was deployed whereas a secondary ion multiplier was used for the detection of  $^6Li$ . Due to the slower signal response of the  $10^{13} \Omega$  amplifier a tau correction (Kimura et al., 2016) was applied for data evaluation.

Measurements of the bracketing standard were performed in raster ablation mode with a scan speed of 20  $\mu m/s$ . The plagioclase profiles were measured in line ablation mode at the rims and raster ablation mode (26  $\mu m$  by 56  $\mu m$ ) further into the grains, with lines and rasters arranged perpendicular to the crystal rim, each line/raster accounting for one measurement value. Individual measurements consisted of 180 cycles with an integration time of 1.049 s per cycle. The first ~35 cycles were used for background correction using only the gas blank reading, followed by ~130

cycles of laser ablation. All analyses that represent one isotopic profile were measured during a single analytical session. As an internal control, the MPI DING reference glass T1-G was measured yielding a long-term reproducibility of 2.1 ‰ ( $\delta^7\text{Li} = 0.4 \text{ ‰}$ , 2 SD,  $n=64$  in 16 sessions during 22 months) in agreement with Steinmann et al., (2019).

#### **Trace element measurements**

Plagioclase trace element concentration profiles were obtained by LA-ICPMS using an Excimer 193 nm (ArF) Resolution (Australian Scientific Instruments) nanosecond laser ablation system coupled to a Nexion2000 (Perkin Elmer, Canada/USA) fast-scanning quadrupole ICPMS, at the Institute of Geochemistry and Petrology, ETH Zürich. The trace element concentration profiles in the plagioclase crystals were measured parallel to the previously analyzed chemical and Li isotopic profiles. The ablation was performed in a S-155 dual-volume ablation cell (Laurin Technic, Australia) under a carrier gas flow consisting of high-purity He (ca.  $0.5 \text{ l.min}^{-1}$ ),  $\text{N}_2$  (cica  $2 \text{ ml.min}^{-1}$ ) and Ar make-up gas (ca.  $1.0 \text{ l.min}^{-1}$ ) from the ICPMS. Line scans were ablated with a spot diameter of  $29 \text{ }\mu\text{m}$ , a repetition rate of 10 Hz, a laser energy density of ca.  $3.5 \text{ J.cm}^{-2}$  and a scan velocity of  $1 \text{ }\mu\text{m.s}^{-1}$ . All concentrations were quantified against the NIST SRM 612 silicate glass wafer as the primary standard (Jochum et al., 2011), using conventional standard-sample bracketing with one line between two standards. The USGS basaltic glass GSD-1G was used as the secondary standard to monitor for the accuracy and reproducibility of the analyses. Both reference materials were ablated with line scans under the same conditions as the unknown samples. The resulting raw intensities were processed using the Igor Pro-based Iolite v2.5 software (Hellstrom et al., 2008), using the implemented data reduction scheme for trace element quantification. The baseline-corrected intensities for each line scan were averaged over integration periods of 5 s (corresponding to 20 mass cycles with a sweep time of 0.25 s each), resulting in a

spatial resolution of 5 µm for the final concentrations along the profiles. We used Si as an internal standard to correct for differences in relative sensitivities, based on the average SiO<sub>2</sub> content of the analyzed plagioclase crystals (63±0.5 wt.%) measured by EPMA. The uncertainties on concentrations at each step of the profiles correspond to the scatter of the 20 measurement cycles integrated within the corresponding time step, quoted at 95% confidence level (2 S.D.).

## **Diffusion modelling**

Diffusion modelling as shown in Fig. 4 was conducted using the diffusion coefficient of Li in an anorthitic plagioclase (Giletti and Shanahan, 1997). Each profile was modelled using a one-dimensional model, and a diffusion exchange at a constant temperature with an infinite medium (core is unaffected by diffusion) is assumed. The shape of the Li concentration profiles as well as the δ<sup>7</sup>Li profiles can be described by an error function. Therefore, the following equation (2) can be applied:

$$C_x = (C_0 - 1) \left( 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right) + 1 \quad (2)$$

where  $C_x$  represents the composition at a distance  $x$  (in µm) from the crystal surface,  $D$  is the Li diffusion coefficient in plagioclase, and  $t$  is the time since the diffusion started.  $C_0$  represents the composition in the core (used values are given in Table S1, S2 and S3). To calculate the timescales for the isotope profiles, the <sup>6</sup>Li and <sup>7</sup>Li are considered as two independent species with different diffusion coefficients. The temperature range used in this study is between 789 °C (sanidine–melt thermometer; Putirka, 2008) to 856 °C (ilmenite–magnetite thermometer; Sauerzapf et al., 2008). Only ilmenite-magnetite pairs passing the equilibrium criteria (Bacon and Hirschmann, 1988) were used for temperature estimations.

## REFERENCES CITED

- Bacon, C.R. and Hirschmann, M.M., 1988, Mg/Mn partitioning as a test for equilibrium between coexisting Fe–Ti oxides: *American Mineralogist*, v. 73, p.57-61.
- Hellstrom, J., Paton, C., Woodhead, J. and Hergt, J., 2008, Iolite: software for spatially resolved LA-(Quad and MC)-ICP-MS analysis Laser Ablation-ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues. P. Sylvester, Editor. Mineralogical Association of Canada:Vancouver. p. 343-348.
- Horn, I., von Blanckenburg, F., Schoenberg, R., Steinhoefel, G. and Markl, G., 2006, In situ iron isotope ratio determination using UV-femtosecond laser ablation with application to hydrothermal ore formation processes: *Geochimica et Cosmochimica Acta*, v. 70, p. 3677–3688, <https://doi.org/10.1016/j.gca.2006.05.002>.
- Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum, K., Frick, D.A., Günther, D. and Enzweiler, J., 2011, Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines: *Geostandards and Geoanalytical Research*, v. 35, p. 397–429, <https://doi.org/10.1111/j.1751-908X.2011.00120.x>.
- Kimura, J.I., Chang, Q., Kanazawa, N., Sasaki, S. and Vaglarov, B.S., 2016, High-precision in situ analysis of Pb isotopes in glasses using 1013  $\Omega$  resistor high gain amplifiers with ultraviolet femtosecond laser ablation multiple Faraday collector inductively coupled plasma mass spectrometry: *Journal of Analytical Atomic Spectrometry*, v. 31, p. 790–800, <https://doi.org/10.1039/C5JA00374A>.

- Longerich, H.P., Jackson, S.E. and Günther, D., 1996, Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation: *Journal of Analytical Atomic Spectrometry*. v. 11, p. 899–904, <https://doi.org/10.1039/JA9961100899>.
- Paton, C., Hellstrom, J., Paul, B., Woodhead, J. and Hergt, J., 2011, Iolite: freeware for the visualisation and processing of mass spectrometric data: *Journal of Analytical Atomic Spectrometry*, v. 26, p. 2508–2518, <https://doi.org/10.1039/C1JA10172B>.
- Paul, B., Paton, C., Norris, A., Woodhead, J., Hellstrom, J., Hergt, J. and Greig, A., 2012, Cell Space: a module for creating spatially registered laser ablation images within the Iolite freeware environment: *Journal of Analytical Atomic Spectrometry*, v. 27, p. 700–706, <https://doi.org/10.1039/C2JA10383D>.
- Steinmann, L.K., Oeser, M., Horn, I., Seitz, H-M. and Weyer, S., 2019, In situ high-precision lithium isotope analyses at low concentration levels with femtosecond-LA-MC-ICP-MS: *Journal of Analytical Atomic Spectrometry*, v. 7, p. 1447-1458, <https://doi.org/10.1039/C9JA00088G>.
- Ubide, T., McKenna, C.A., Chew, D. M. and Kamber, B.S., 2015, High-resolution LA-ICP-MS trace element mapping of igneous minerals: in search of magma histories: *Chemical Geology*, v. 409, p. 157–168, <https://doi.org/10.1016/j.chemgeo.2015.05.020>.
- Ubide, T., Mollo, S., Zhao, J.X., Nazzari, M. and Scarlato, P., 2019, Sector-zoned clinopyroxene as a recorder of magma history, eruption triggers, and ascent rates: *Geochimica et Cosmochimica Acta*, v. 251, p. 265–283, <https://doi.org/10.1016/j.gca.2019.02.021>.



**TABLE S1. Time scales of Li diffusion from Li concentration in plagioclase crystals from MFT and boundary conditions for each profile. Timescales are calculated for 789°C and 856°C using D of  $1.05 \times 10^{-11} \text{ m}^2/\text{s}$  and  $2.79 \times 10^{-11} \text{ m}^2/\text{s}$ , respectively.**

Grain	Line	C <sub>0</sub> . Core (ppm)*	Rim (ppm)*	789 °C		856 °C	
				Time (min)	S.D.	Time (min)	S.D.
7	L1	20.2	5.3	3.0	0.5	1.5	0.5
	L2	19.6	6.7	3	1	1.0	0.2
11	L1.1	27.7	6.2	5	1	2.0	0.6
	L1.2	28.3	5.9	2.5	1.0	1.0	0.3
13	L1.1	27.2	5.0	6.5	0.5	2.0	0.5
	L1.2	30.0	6.8	6.0	1.0	2.0	0.2
15	L2.1	27.8	5.1	7	2	2.5	1
	L2.2	28.6	6.4	6	2	2.0	0.5
	L3.1	25.6	4.9	3	1	1	0.2
	L3.2	21.1	6.5	3	1	1	0.2
21	L1.1	20.1	6.7	1	0	0.3	0.1
	L1.2	22.3	8.5	1	1	0.3	0.1
	L3.1	28.6	7.7	3	1	1	0.2
	L3.2	28.7	7.4	4	2	1.5	0.5
25	L1	23.6	8.8	2.5	0.5	0.8	0.3
	L2	23.6	7.0	7	1	2.5	0.5
27	L1	23.4	6.2	13	2	4.5	1
	L2	28.4	8.4	3	1	1	0.5

Note: Samples are stored in the collection of ETH Zurich, Department of Earth Sciences, Zurich, Switzerland.

\*Measured using a LA-ICPMS

**TABLE S2. Time scales of Li diffusion from  $\delta^7\text{Li}$  profiles in plagioclase crystals from MFT and boundary conditions for each profile. Timescales are calculated for 789°C and 856°C using D of  $1.05 \times 10^{-11} \text{ m}^2/\text{s}$  and  $2.79 \times 10^{-11} \text{ m}^2/\text{s}$ , respectively.**

Grain	Line	C <sub>0</sub> - Core ( $\delta^7\text{Li}$ ) <sup>*</sup>	Rim ( $\delta^7\text{Li}$ ) <sup>*</sup>	789 °C		856 °C	
				Time (min)	SD	Time (min)	SD
7	L1	-9.1	-0.8	7.5	1	2.8	0.2
11	L1.1	-2.6	3.2	2.5	1	0.7	0.2
13	L1.1	-9.2	-1.2	1.5	1	0.5	0.5
15	L2.1	-1.4	0.7	0.5	0.1	0.2	0.1
21	L1.1	-7.0	-3.8	1	0.5	0.5	0.1
21	L3.1	-9.0	-1.9	5	1	1.5	0.5
25	L1	-7.0	2.9	13	5	5	2
27	L1	-8.3	2.6	15	3	6	2

Note: Samples are stored in the collection of ETH Zurich, Department of Earth Sciences, Zurich, Switzerland.

<sup>\*</sup>Measured using a fs-LA-MC-ICPMS

**TABLE S3.** Time scales of Li diffusion from  $\delta^7\text{Li}$  profiles in plagioclase crystals from MFT and boundary conditions for each profile. Timescales are calculated for 789°C and 856°C using D of  $1.05 \times 10^{-11} \text{ m}^2/\text{s}$  and  $2.79 \times 10^{-11} \text{ m}^2/\text{s}$ , respectively. The highest and lowest Li isotopic value within the error are taken as boundary conditions for the diffusion modelling.

Grain	Line	C <sub>0</sub> - δ <sup>7</sup> Li Core (‰)*	δ <sup>7</sup> Li Rim (‰)*	789 °C	856 °C
				Time (min)	time (min)
<u>upper values</u>					
7	L1	-10.9	1.5	12	6
11	L1.1	-4.4	5.7	4	1.5
13	L1.1	-11.2	1.2	3.5	1.1
15	L2.1	-3.6	3.0	0.75	0.3
21	L1.1	-7.4	-1.7	0.75	0.3
21	L3.1	-11.0	1.0	8.5	3.25
25	L1	-9.0	5.1	16	6
27	L1	-10.1	5.0	30	12
<u>lower value</u>					
7	L1	-7.3	-3.0	4.5	1.6
11	L1.1	-0.7	0.8	1	0.35
13	L1.1	-7.1	-3.6	0.9	0.4
15	L2.1	-1.6	0.8	0.3	0.1
21	L1.1	-2.7	-5.9	0.15	0.05
21	L3.1	-7.0	-4.7	2.75	1
25	L1	-5.1	0.6	5.5	2.2
27	L1	-6.5	0.1	10	4

Note: Samples are stored in the collection of ETH Zurich, Department of Earth Sciences, Zurich, Switzerland.

\*Measured using a fs-LA-MC-ICPMS